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METHOD FOR MANUFACTURING STYRENE GROUP POLYMER WITH HIGH WATER ABSORPTION AND WATER RETENTION

[KODO NO SUIKYUSHUSEI OYOBI HOSUISEI O YUSURU SUCHIRENKEI JUGOTAI NO SEIZOHO]

HIROTAKA MIYATA

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INVENTOR(S)	(72):	HIROTAKA MIYATA
APPLICANT(S)	(71):	Daicel Chemical Industries, Ltd.
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Specification

1. Title of the Invention

Method for Manufacturing Styrene Group Polymer with High Water Absorption and Water Retention

2. Scope of Patent Claims

A method for manufacturing a styrene group polymer with high water absorption and water retention, characterized in that an acrylonitrile-styrene copolymer with a number average molecular weight of 5,000 or more and an acrylonitrile content of 20 to 30 wt % is treated with rich sulfuric acid with a concentration of 75 to 98 %; and the sulfur-treated product obtained is changed to an alkali metal salt, if necessary.

3. Detailed Description of the Invention

The present invention pertains to a method for manufacturing a new polystyrene group polymer that absorbs a large amount of water, is swollen, and retains water.

[1] Numbers in the margin indicate pagination in the foreign text.

More specifically, the present invention pertains to a method for manufacturing a styrene group polymer with high water absorption and water retention as a sulfuric acid-treated product of an acrylonitrile-styrene copolymer or its alkali metal salt.

Recently, various kinds of polymers with high water absorption in which synthetic and semisynthetic polymers are used as a base have been developed and put into practice. For example, there is hydrolysate of polyacrylonitrile, crosslinked carboxymethyl cellulose, crosslinked polyvinyl alcohol, crosslinked hydroxyethyl methacrylate, hydrolysate of starch-acryl graft body, etc. However, inexpensive compounds with high water absorption and water retention having a molecular structure, like the styrene group polymer being obtained in the present invention, have not been developed, yet. It has already been known that compounds, which are modified with acrylamide and/or acrylic acid or acrylic acid metal salt and have hydrophilicity and water absorption in Japanese Kokoku Patent Nos. Sho 49[1974]-46199, Sho 52[1972]-42916, et cetera.

On the other hand, it is described in "Ion Exchange" written by Masatate Honda that sulfonated polystyrene in

which polystyrene is sulfonated has hydrophilicity and water

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absorption.

In addition, a method that sulfonates a ternary copolymerized resin of acrylonitrile-styrene-crosslinking monomer (a resin in which a composition containing styrene monomer and acrylonitrile monomer at 20 parts by weight or less to a crosslinking monomer at 100 parts by weight) and manufactures an ion exchange resin is described in Japanese Kokoku Patent No. Sho 58[1983]-10543. However, its purpose is to manufacture an ion exchange resin with high crosslinking and low water absorption because of the ternary copolymerized product with the crosslinking monomer, which is essentially different from an intended polymer with high water absorption of the present invention.

This inventor discovered that when a copolymerized product of acrylonitrile and styrene was used as a starting substance and simultaneously subjected to a hydrolysis and a sulfonation through a sulfuric acid treatment, an inexpensive styrene group polymer with high water absorption and water retention having a new molecular

structure could be obtained. The present invention was then completed.

In the method of the present invention, in case polyacrylonitrile or polystyrene itself is used as a starting raw material, the space between the molecules and in the molecules is small, and high water absorption is difficult to be expected. However, with the copolymerization, since the space between them molecules and in the molecules is widened, higher water absorption can be expected. This is a ground for the use of the acrylonitrile-styrene copolymer as a starting raw material. Therefore, a copolymer with a composition close to an azeotropic composition (an acrylonitrile content of 25 wt %) of acrylonitrile and styrene, that is, an acrylonitrile-styrene copolymer with an acrylonitrile content of 20-30 wt % is a preferable copolymer as a starting raw material of the present invention.

In addition, it is well known that this acrylonitrile-styrene copolymer is also utilized as a plastic with excellent properties such as transparency, heat resistance, toughness, impact resistance, and chemical resistance in which the drawbacks of the polystyrene are improved. For the use as a plastic, a copolymerization composition with an acrylonitrile content of 20 to 30 wt % to utilize the

aforementioned properties is on the market. Therefore, a copolymer with an acrylonitrile content of 20 to 30 wt % is preferable in terms of economy. Moreover, as the molecular weight of the starting raw material, a number average molecular weight of 5,000 or more meets the purpose of the present invention. The reason for this is that if a copolymerized resin with a number average molecular weight of less than 5,000 is used as the starting raw material, the sulfuric acid-treated product or its alkali metal salt obtained has solubility in water, causing a difficulty in obtaining high water absorption and water retention as the objective of the present invention. Furthermore, copolymers for plastics on the market have a number average molecular weight of about 50,000, and they are preferable as the starting raw material of the present invention in terms of molecular weight.

The method for polymerizing the acrylonitrile-styrene copolymer of the present invention may be any method of bulk polymerization, emulsion polymerization, suspension polymerization, solution precipitation polymerization, et cetera, and a polymerized product with a pearl shape or powder shape and with a porous shape through the extraction of an unreacted monomer is preferable in terms of infiltration and swelling of the reaction agent.

As the reaction treatment agent for the sulfuric acid treatment, rich sulfuric acid with a concentration of 75-98 wt % is used to be able to obtain the intended product of the present invention. If the sulfuric acid concentration is less than 75 wt %, a polymer with high water absorption cannot be obtained. With the treatment with the rich sulfuric acid, acrylonitrile in the acrylonitrile-styrene copolymer is partially hydrolyzed, and styrene can be partially sulfonated, generating an intended styrene group polymer with high water absorption.

As the sulfuric acid treatment conditions of the acrylonitrile-styrene copolymer of the present invention, the reaction temperature is 20 to 130°C, the time is 0.5 to 3 h, and the charge ratio of solid/liquid (the ratio of acrylonitrile-styrene copolymer/rich sulfuric acid) is optically changed in a range of 1/5 to 1/40 to be able to set optional high water absorption.

If the reaction temperature is lower than 20°C, the reaction velocity is slow, and high water absorption is difficult to be obtained. On the other hand, if the reaction temperature is higher than 130°C, the acrylonitrile-styrene copolymer is easily dissolved in the

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reaction agent. Both cases are not preferable. Therefore, the reaction temperature is preferably 20 to 130°C.

If the reaction time is shorter than 0.5 h, the reaction is insufficient, and high water absorption cannot be obtained. If the reaction time is within 3 h, since the reaction is sufficiently advanced, 0.5 to 3 h is preferable.

If the charge ratio of solid/liquid exceeds 1/5, since the reaction agent cannot be sufficiently infiltrated, swollen, and reacted up to the center of the pearl-shaped or powder-shaped polymerized product, high water absorption cannot be obtained. On the other hand, if the charge ratio is smaller than 1/40, the polymerized product is easily dissolved in the reaction agent, and the infiltration and swelling reaction as the characteristic of the method of the present invention is difficult to be carried out. Therefore, the charge ratio of solid/liquid is preferably 1/5 to 1/40. In addition, if necessary, the sulfuric acid-treated product of the acrylonitrile-styrene copolymer obtained by the aforementioned reaction treatment is immersed into an aqueous alkali metal salt solution, thus being able to obtain an alkali metal salt of the sulfuric acid-treated product of the acrylonitrile-styrene copolymer.

The new styrene group copolymer obtained by the method of the present invention has high water absorption and water retention, prevents sanitary materials such as sanitary goods and paper diapers from being too wetted with water, or is appropriately used as a material for agriculture and forestry and horticulture for rendering water retention to lands with weak water retention power, dehydrator from organic substances such as solvent, perfume preservative for sustaining an indoor aromatic over a long term, sealant, fire-extinguishing agent, anti-dewing agent, antistatic agent, et cetera.

Next, the present invention will be explained in detail by application examples.

Application Example 1

A bead with a number average molecular weight of 50,000 having a copolymerization composition of 25 wt % acrylonitrile and 75 wt % styrene was manufactured. The residual monomer was extracted with vapor, and 100 g bead with a mesh of 40 to 80 was obtained by a vibratory screen machine. This bead was injected into 1 kg aqueous solution with a sulfuric acid concentration of 80 wt % in a beaker made of glass and reacted at 80°C for 1 h. With a lapse of time, sulfuric acid was absorbed in the copolymerized bead,

swollen, and reacted to obtain a yellowed bead. In this process, the volume of the bead was increased to about 1 L.

Next, this yellowed bead was mixed with a large amount of water, and the unreacted sulfuric acid was removed by washing. As the degree of washing, the volume of the bead was further increased. The hydrogel obtained in this manner was dried at 80°C for 3 h, so that a slightly yellowed dried bead was obtained. When an infrared absorption spectrum analysis of this bead was carried out, the absorption of the acrylonitrile group at 2,220 cm^{-1} was reduced to a shoulder degree, and the absorption based on acrylamide and acrylic acid were seen at 1,660 cm^{-1} and 1,710 cm^{-1}, confirming that the acrylonitrile was hydrolyzed. In addition, the absorption of sulfonic acid was generated at 1,210 to 1,010 cm^{-1}, confirming the generation of sulfonated styrene.

The aforementioned water-washed and swollen hydrogel was ion-exchanged with a prescribed caustic soda and a prescribed caustic potassium and converted into a sodium salt type and a potassium salt type. In this manner, reaction products of acid type, sodium type, and potassium type were obtained.

Application Examples 2 through 4

Copolymerization compositions similar to that of Application Example 1 were reacted under chemical reaction conditions as shown in Table 1, washed, and dried, so that reaction products of an acid type were obtained.

Application Examples 5 through 8

A bead with a number average molecular weight of 40,000 having a copolymerization composition of 30 wt % acrylonitrile and 70 wt % styrene was reacted as shown in Table 1 by methods similar to those of Application Examples 1 and 2 through 4, washed, and dried, so that reaction products of an acid type were obtained.

Application Example 9

1 g each of the treated products (sample Nos. 1-1 to 1-3) of Application Example 1 was immersed into water of pH = 10, pH = 7, and pH = 4, 1 wt % saline solution, 3 wt % saline solution, and 100 g human urine and held for 1 h, and the amount of saturated water absorption was measured. The results obtained are shown in Table 2.

From Table 2, it is understood that since the styrene

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group polymer of the present invention is ionic, it has high water absorption, though it is extremely affected by the ionic property of the solutions.

Application Example 10

1 g each of the reaction products (sample Nos. 2-8) of Application Examples 2 through 4 and 5 through 8 was immersed into 300 g water of pH = 7 and held for 1 h, and the amount of saturated water absorption was measured. In addition, the saturated water-absorbed hydrogels were applied to a centrifugal separator at 2,000 rpm for 1 min, and the amount dehydrated was measured to calculate the water retention (the amount of water retained). The results obtained for the water absorption and the water retention are shown in Table 3.

From Table 3, it is understood that the styrene group polymer of the present invention has high water absorption and water retention.

Comparative Example 1

A copolymerization composition similar to those of Application Examples 2 through 4 was reacted under chemical reaction conditions as shown in Table 1, washed, and dried, so that a reaction product of an acid type was obtained. For the reaction product obtained, the water absorption and the water retention were measured by the methods of Application Example 10. The results obtained are shown in Table 3.

Comparative Example 2

A crosslinked bead with a number average molecular weight of 90,000 having a ternary copolymerization composition of 13 wt % acrylonitrile, 77 wt % styrene, and 10 wt % divinylbenzene was manufactured by a suspension polymerization. This bead was reacted under chemical reaction conditions as shown in Table 1, washed, and dried, so that a reaction product of an acid type was obtained. For the reaction product obtained, the water absorption and the water retention were measured by the methods of Application Example 10. The results obtained are shown in Table 3. From Table 3, it is understood that since this reaction product has a crosslinked structure, the water absorption and the water retention are very low.

Table 1: Compositions and reaction conditions of acrylonitrile-styrene copolymers

表−1 アクリロニトリル−スチレン共重合体の組成と反応条件

1 実施例および比較例の番号		2 サンプル番号	3 アクリロニトリル/スチレン共重合体組成	4 数平均分子量	5 反応条件 7 硫酸濃度(%)	8 温度(℃)	9 時間(hrs)	10 酸/粒 仕込比	6 型
11 実施例	1	1−1	25/75	50,000	80	80	1	1/10	14 [illegible]
	1	1−2							
	1	1−3							
	2	2					2		15 [illegible]
	3	3			92	90	3		
	4	4					2	1/20	
	5	5	30/70	48,000	82	85	1	1/10	
	6	6					2		
	7	7			98	98	3		
	8	8					2	1/20	
12 比較例	1	9	25/75	52,000	40	80	1	1/10	16 [illegible]
	2	10	13 完全共重合体	73,000	60	70	1	1/10	

1. Application example and comparative example No.

2. Sample No.

3. Acrylonitrile/styrene copolymerization composition

4. Number average molecular weight

5. Reaction condition

6. Type

7. Sulfuric acid concentration (%)

8. Temperature (°C)

9. Time (h)

10. Solid/liquid charge ratio

11. Application Example

12. Comparative Example

13. Ternary copolymer

14. Acid type

    Na type

    K type

15. Acid type

16. Acid type

Table 2: Composition and water absorption of absorbing solutions (g/g)

表－2 吸収液の種類と吸水性（g/g）

吸収液の種類 ＼ サンプル番号	1－1	1－2	1－3
pH＝10の水	55	27	27
pH＝7の水	55	50	18
pH＝4の水	34	27	37
1％食塩水	16	14	12
3％食塩水	15	10	[illegible]
人尿	25	20	14

1. Sample No.

2. Kind of absorbing solution

3. Water of pH = 10

   Water of pH = 7

   Water of pH = 4

   1 % saline solution

   3 % saline solution

   Human urine

Table 3: Water absorption and water retention (g/g)

表－3 吸水性および保水性（g/g）

特性	サンプル番号								
	2	3	4	5	6	7	8	9	10
pH＝7の水の吸水量	85	140	225	45	60	125	220	10	0.7
保水性	65	120	200	35	55	105	180	4	0.2

1. Characteristic

2. Sample No.

3. Amount of water absorption of water of pH = 7

4. Water retention